COATINGS

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TRENDS IN CONTEMPORARY METHODS FOR DECORATION OF GLASS AND GLASS ARTICLES (A REVIEW)

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The main trends in up-to-date methods for decorating glass and glass articles are considered. A glass decoration method using plasma spraying of glass tubing is proposed.

Decorative coatings are deposited on glass articles to improve their aesthetic parameters. According to GOST 30407–96, a decorative coating can be deposited on a product in the form of decalcomania, painting, drawing, or coating (partial or continuous) using silicate paints, compounds of precious and other metals, diffusion coloring, or low-melting glass. Methods for decorating glass articles in the cold and hot state are regulated by standard GOST 24315–80.

However, the existing standardizing documents do not reflect all up-to-date decoration methods, such as non-fired coatings, deposition of decorative materials using nontraditional power sources, etc.

This study considers the main trends in contemporary glass-decorating methods in Russia and abroad.

The Gusevskii Cut Crystal Works is justifiably regarded as the leader in this sphere in our country. Having survived a period of depression and hardships in the 1990s, the company has maintained its ability to satisfy the demands of domestic consumers. Having acquired high-efficiency imported machinery, the Gusevskii Woks started producing wine and liqueur glass of fashionable designs. Popular classical methods for decorating glass articles have been revived and new methods have been implemented [1]. The Gusevskii Works used to produce glass articles imitating malachite, opal, aquamarine, alabaster, turquoise, aventurine, and blue and red marble. The formulas of these glasses have not been lost and are gradually brought back into production. The company has revived the technology of melting tinted glasses using oxides of rare-earth elements. Diamond crystal cutting is implemented according to particular patterns representing a particular flower or a plant, etc. This decorative technique is not found abroad. Highly artistic products decorated by deep etching on multilayer glass in the modernist style of E. Halle (France) enjoy great popularity [2].

The "huta" decoration technique remains an important line in the development of highly artistic articles with new decorative elements [3]. Articles made of flashed and tint glasses continue to be very popular. Articles blown of laminated (flashed) glass have a richer color palette and are very picturesque. Production of fancy articles of tinted glass is promising as well. This primarily includes handmade techniques and huta technology with various types of decoration [4]. Researchers are developing tint glasses of a new color range tinted simultaneously with cadmium sulfide and chromium sulfide [5]. Contemporary huta technology as well implies a wide range of specific decoration techniques, such as color glass crumb, glass drops, and "ariel" and "grail" stamping. The latest achievements include spiral wire decoration and the watercolor drip technique [6, 7].

Extensively used methods for decorating glass in a cold state with silicate paints include decalcomania, silk-screen printing, painting on glass, aerography, and relief printing (stamping).

Foreign technology of silk-screen printing on glass is constantly being upgraded. The PLM Redfean Company (Great Britain) has developed and implemented the Kaleidocoat technology for printing glass articles in different colors [8]. Manufacturers in Great Britain use the Premium Print silk-screen printing machine providing for a printing accuracy of ≤ 0.2 mm, which improves the precision of depositing patterns and inscriptions using up to 6 colors [8]. A special technology involves using special pastes deposited on glass by thermoplastic imprint intended for fast IR and UV drying [9].

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Such decoration method as painting on glass has not lost its significance. This method currently uses silicate, lustrous, foaming, and icy paints. Foaming paints are silicate paints which swell and partly exfoliate from the article in firing. A decorative effect consists in intensifying the relief of the pattern. Icy paints are flux granules of size 100 – 150 nm that are deposited on glass previously coated by a burning-out adhesive. The granules become fused and rounded in firing and thus create a unique decorative effect [10, 11]. Grisaille and crackelage are original varieties of decoration by painting. Grisaille is widely used nowadays. The specific feature of this method is creating patterns from different shades of a single color, mostly brown or black. Crackelage is a decoration method using silicate paints, in which a pattern on glass has fine fused cracks [11, 12].

Some foreign companies use relief decoration of glass using volumetric paints (a variant of painting) with high-relief elements up to 3000 nm high. To perform relief decoration of glass articles, syringes filled with paste based on silicate paints are used in the industry [13]. The Berezhanskii Glass Works (Ukraine) has developed and implemented a technology for melting tinted volumetric paints to decorate household glassware using relief decoration. These paints are currently used to produce fancy glass products [14]. Paint compounds producing the crackle effect and the "running" and "wavy" line effect are very popular [13].

A relatively new method for depositing silicate paints on various-purpose glass is "flask plating." A glass article on a conveyor belt is transported through a vertically poured "paint curtain." The surface of the glass is rapidly and uniformly covered by a layer of paint, which is not sprayed, but circulates inside the coloring system. After drying, the glass is fired to fix the coating [9].

A highly efficient method is applying silicate paint by aerography. Aerography is the only method making it possible to obtain a "descending" or "ascending" coating. A descending coating is one where the main color tone of the decorative layer becomes diluted toward the bottom of the article and an ascending coating is one in which the color intensity decreases toward the top of the article [10 – 12].

Glass articles can be decorated as well by deposition of colored metal-oxide coatings and films of precious metals. Depending on the way of applying metal oxide coatings on glass, such methods are classified as spray coating, iridization, lustrous paint coating, and thermovacuum coatings [10 – 12].

Iridization is implemented using salts of tin, bismuth, barium, titanium, strontium, indium, etc. Iridization can be high-temperature or low-temperature. A metal oxide film deposited on glass appears colorless in passing light, but gleams with all rainbow colors in reflected light [10, 11].

A popular method is decoration with lustrous paints that are solutions of chlorides of heavy metals. Thus, mother-of-pearl coatings obtained by depositing mixtures of tinted and clear luster paints impart a new look to the product, making it attractive to customers. Lustrous paints make it possible to create decorative coatings with a "marble look" [10 – 12].

In view of the extensive use of household microwave ovens, a technology has been developed for depositing metal oxide coatings on fire-resistant aluminoborosilicate glassware, which has good colorist parameters and high chemical resistance [15].

Domestic customers have high demand for glassware for food and drinks decorated with films of precious metals. This decoration technology produces decoration known as stamped gold. In this case a gold-bearing compound is applied to a dull glass surface and heat-treated. Analysis of household glass sold in 2001 – 2002 indicates that products made in the Czech Republic, Germany, and France have diverse golden coatings.

Intense research is carried out to improve the existing techniques and to develop new ones for decorating articles with precious metals. A study in [16] describes a refined technology of decorating articles using gold. The Zerdek Company (Germany) offers a wide range of compounds containing precious metals for decoration: glossy gold, glossy lemon gold, glossy platinum, polishing gold, polishing platinum, polishing silver, powdered white gold, powdered platinum, powdered silver and gold for microwave treatment, gold for heat treatment [13].

The world practice of household glass decoration extensively uses fire-free coatings based on organic compounds. This group included polyurethane composites, epoxy resins, lacquers, and paints.

However, an essential disadvantage of these coatings compared to coatings based on silicate paints is their low service parameters. Consequently, these coatings cannot compete with silicate ones but make it possible to expand product ranges and product designs [17].

A promising line is using nontraditional power sources (laser beam, low-temperature plasma) for decorative treatment of glass and glassware [10, 18, 19].

A plasma decoration technology developed by us involves deposition of coatings based on silicate glasses on products in a cold or a hot state. Decoration was performed on wine and liqueur glasses produced by the Krasnyi Mai Glass Works. The decorating materials was glass tubing of diameter 1.0 – 3.0 mm, which is generated in substantial quantities in the manual production of glassware and is essentially a kind of waste. Tubing up to 1.5 mm in diameter is recommended for decorating glassware in a cold state, and tubing up to 3 mm for decorating glassware in a hot state.

Decoration was implemented using an UPU-8m arc plasma gun. The operating conditions of the plasma gun were as follows: working voltage 30 – 32 V, current strength 400 – 450 A. Argon was the plasma-forming gas with a flow rate of 2.0 – 2.5 m^3/h. The distance from the plasma burner nozzle to the surface of a cold glass article in plasma spraying of glass tubes was 450 – 500 mm, and the distance from a glass article heated to a temperature exceeding the soften-

ing point was 250 – 350 mm. Glass tubing was fed to the GN-5r plasma burner by hand or automatically at a rate of 2.0 – 5.0 mm/sec depending on the average diameter of the tubes. Spraying of glass tubing generates particles 80 – 300 nm in diameter, which deform upon colliding with the glass substrate and produce a high-quality decorative surface.

Glass tubing for decoration was taken from milky glass (wt.%): 66.6 SiO_2, 6.3 Al_2AO_3, 6.3 CaO, 14.8 Na_2O, 1.0 K_2O, 5.0 F, and blue cobalt-tinted household glass (%): 68.6 SiO_2, 6.3 Al_2O_3, 9.3 CaO, 14.8 Na_2O, 1.0 K_2O, 0.002 Co. Decoration of glass articles with a surface area of 80 – 100 cm^2 lasted on the average 50 – 130 sec.

The advantage of this decorating method compared to other known methods is the possibility of consecutive deposition of decorative layers of various tints and shades on a glass substrate or simultaneous deposition of a multi-colored composition depending on the artist's purpose. High efficiency and environmental safety make this method ideal for wide industrial implementation.

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